

The Rate of Solution of Hydrogen by Palladium.

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In two recent communications* the view has been advanced that in hydrogen-palladium the dissolved gas cannot be regarded as homogeneously distributed, and that solution takes place through the medium of an amorphous metallic phase which acts as a vehicle for the transference of gas to the crystalline metal. Experiments have been described from which it is concluded that in hydrogen-palladium one is dealing with a case of simultaneous adsorption and solution (or sorption), since as soon as any gas is adsorbed solution begins through diffusion from the adsorbed layer.

The adsorption equilibrium would be rapidly established, too quickly, perhaps, for any record of its rate to be measured, but could such observations be made it might be expected that the following relation would hold:—

$$dc/dt = kC^n,$$

where C is the concentration in the adsorbed layer and k and n constants depending on the nature of the adsorbent and the substance adsorbed, the rate of adsorption of a gas at constant pressure varying with the concentration of the gas in the adsorbed layer. If, therefore, the adsorbed layer is maintained at constant concentration by surrounding it with an unlimited supply of gas at constant pressure, the rate of inward diffusion from it could be measured. Thus a complete rate of solution curve should consist of two portions, the first representing adsorption and the second inward diffusion, the two coinciding when the rate of adsorption equals the rate of diffusion.

Should there be no adsorption, or should the dispersivity be so great that the metal may be regarded entirely as surface, then only one phenomenon would be present, and a curve representing the rate of solution of gas should show no discontinuity of curvature. It might, of course, be impossible to observe the changes of rate with concentration for the initially adsorbed gas, since adsorption is usually regarded as an exceedingly rapid process, and

* Holt, Edgar, and Firth, 'Zeit. Phys. Chem.,' vol. 82, p. 5 (1913), and Andrew and Holt, 'Proc. Roy. Soc.,' A, vol. 89, p. 170 (1913).

hence a smooth rate-concentration curve need not necessarily imply the absence of all but one phenomenon.

It has already been mentioned that there is evidence that solution of gas takes place through the intermediary of an allotropic and probably amorphous phase of the metal. The solubility of hydrogen in this phase (which throughout this paper will be called α -palladium, the other phase being called β -palladium) may be far more rapid than in the stable β -variety, though the solubility of hydrogen in the two forms may be nearly the same. Were this the case, then a rate-concentration curve should at first give values for the solution in α -palladium until this rate had decreased to and equalled that in the β -modification, the subsequent portion of the curve representing the change of concentration per unit time in this latter form of the metal.

The graphs obtained under these conditions would resemble in their general form those for simultaneous adsorption and solution, except that the first portion of the curve would be more drawn out, since it is highly improbable that saturation of α -palladium would take place as rapidly as true adsorption. There is, however, no real distinction except in degree between the two cases. If one imagines the α -metal as a film on a mass of the β -form, then if the rate of solution of gas in α - and β -palladium is very different, the phenomenon of adsorption might be simulated.

In the present communication an attempt has been made to determine the rate of solution-concentration curves for hydrogen at constant pressure in different forms of palladium and under different conditions, in order to investigate further the phenomenon of the solution of hydrogen in this metal. The apparatus employed is illustrated in fig. 1.

The palladium was contained in the bulb A which, by means of the three-way tap B, could be put into communication either with the pump, or with the supply of hydrogen, or with the long tube CD, which ended in the

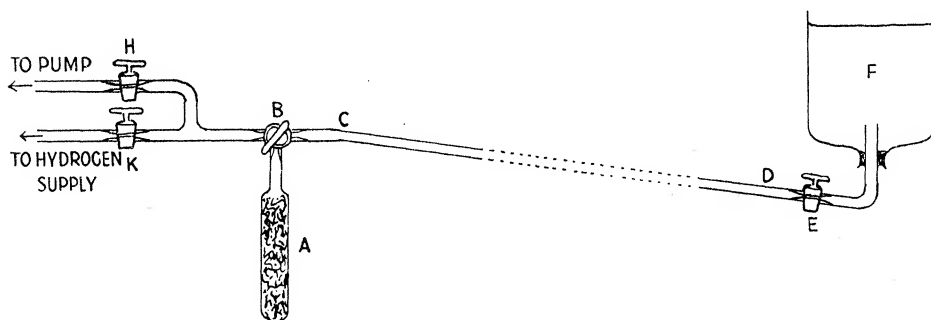


FIG. 1.

reservoir F, and was filled with a liquid paraffin of low vapour pressure. The tube CD had a uniform bore of about 4 mm., and was somewhat more than 400 cm. in length. It was graduated throughout its entire length, and was somewhat raised at one end so as to ensure a sharp meniscus to the liquid running up it.

The method of conducting an experiment was as follows:—A weighed amount of metal was sealed in the bulb A, and, the reservoir F being empty, the air through the apparatus was at atmospheric pressure. The tap K was then closed, and B turned so as to permit the evacuation of the space HKB by the pump. This being accomplished B was further turned, and the dead space in A evacuated, its volume being determined by reducing the collected gas to N.T.P. The taps H and B being now shut, hydrogen was allowed to fill the space HKB, A meanwhile remaining evacuated. The reservoir F being now filled with liquid, E was opened, and a stream of hydrogen passed through CD for several hours so as to displace completely the air it contained. Finally the tap K was shut, and the position of the liquid in CD being noted on the scale, B was turned so as to place the metal in contact with the gas in CD.

The liquid at once moved rapidly along the scale on account of the vacuum in A, but the volume of the dead space having been determined in terms of scale divisions along CD, the point at which readings of the rate of solution could be commenced was at once ascertainable.

The rate measured was the time taken by the liquid to travel one division on the scale, and determinations were made throughout its length at points representing known concentrations of gas in the metal. The gas was maintained at an almost constant pressure during the experiment, since the diameter of the reservoir F was so great that the total volume of liquid required to fill the tube CD did not alter the surface level by more than a few millimetres, and the specific gravity of the paraffin employed being somewhat less than that of water, the small apparent error arising from changes in the level of the liquid in F was diminished.

The solution of gas in the metal caused a rise of temperature in A which operated in two ways, on the one hand hastening the rate of occlusion by heating the metal, on the other hand expanding the gas in A and causing a check to the rate at which the liquid would travel along CD. The former of these effects was obviated as far as possible by placing A in a water-bath at constant temperature, while the latter was rendered quite negligible by making the dead space in A so small in comparison to the volume of CD that any expansion of the small volume would have no material effect on the total volume of gas in the apparatus.

A further source of error might arise from the viscosity of the liquid causing a lag in the rate of its advance along the scale during a period of rapid occlusion of gas. Some experiments were therefore carried out with different liquids, but though the viscosity has an undoubted effect in any one experiment, it caused little error in the relative values of a series.

The following tables contain a summary of the results obtained with palladium black, very thin foil 0.004 mm., and foil about 0.2 mm. thick.

Table I.—Palladium Black. Temperature 15° C.

(1)		(2)	
Volume of gas occluded by 1 vol. of metal.	Time for one division of scale.	Volume of gas occluded by 1 vol. of metal.	Time for one division of scale.
	secs.		secs.
112	0.3	112	0.3
162	0.6	162	0.6
212	1.6	212	1.3
232	2.8	262	3.2
252	4.2	282	4.5
272	8.6	312	11.0
292	21.0	332	32.0
312	48.0		

Table II.—Foil 0.004 mm. thick.

Temperature 15° C.				Temperature 83° C.	
(1)		(2)		(3)	
Volume of gas occluded by 1 vol. of metal.	Time for one division of scale.	Volume of gas occluded by 1 vol. of metal.	Time for one division of scale.	Volume of gas occluded by 1 vol. of metal.	Time for one division of scale.
	secs.		secs.		secs.
11	3.0	5	1.0	11	0.6
22	4.6	22	4.0	33	1.4
33	5.6	33	4.8	55	1.8
55	6.6	55	6.2	77	2.4
88	7.0	88	10.0	99	2.5
121	7.4	99	11.6	121	3.2
143	8.0	110	15.0	143	4.4
176	8.2	121	19.0	165	6.0
209	9.0	132	23.0	187	8.0
220	9.6			209	13.5
242	10.6				
264	13.6				
286	16.0				
308	23.0				
330	37.0				

Table III.—Foil about 0.2 mm. thick.

Temperature 15° C.						Temperature 70° C.	
(1)		(2)		(3)		(4)	
Volume of gas occluded by 1 vol. of metal.	Time for one division of scale.	Volume of gas occluded by 1 vol. of metal.	Time for one division of scale.	Volume of gas occluded by 1 vol. of metal.	Time for one division of scale.	Volume of gas occluded by 1 vol. of metal.	Time for one division of scale.
	secs.		secs.		secs.		secs.
40	8.0	40	13.0	40	32.8	40	6.4
74	8.6	74	13.2	74	56.0	74	7.2
108	10.4	108	14.0	108	67.4	142	7.6
142	12.4	176	15.6	142	76.4	176	8.2
210	15.0	210	16.8	176	88.0	210	9.2
244	16.0	244	18.4	210	95.0	244	9.4
278	16.9	278	19.2			278	10.6
312	17.9	312	20.4			312	12.6
346	19.4	346	23.0			346	14.0
380	22.4	380	25.8			380	15.8
414	25.5	414	29.4			414	18.4
482	39.6					448	22.6
						516	41.0

Table IV.—Foil about 0.2 mm. thick.

Metal cooled in hydrogen after heating <i>in vacuo.</i>		Metal cooled in hydrogen after heating in hydrogen.	
Volume of gas occluded by 1 vol. of metal.	Time for one division of scale.	Volume of gas occluded by 1 vol. of metal.	Time for one division of scale.
	secs.		secs.
40	4.2	6	5.8
74	4.4	40	5.6
108	6.8	74	14.2
176	12.6	108	76.0
210	22.0	123	108.0
244	28.4		
278	32.0		
312	33.4		
346	37.6		
380	42.2		
414	47.0		

By the use of the metal in different states it was hoped that any effect due to variation of dispersivity might be detected, while palladium black served also to form a comparison between α - and β -metal, since the black was believed to consist mainly of the α -form.

In the preceding tables only one specimen of palladium black and thick or

thin foil was employed for the various experiments with each form of the metal.

The data contained in the above tables are represented by graphs in figs. 2, 3, 4, and 5, which correspond with Tables I, II, III, and IV respectively, but for convenience in arranging the curves the values for Nos. 2 and 3 in fig. 3

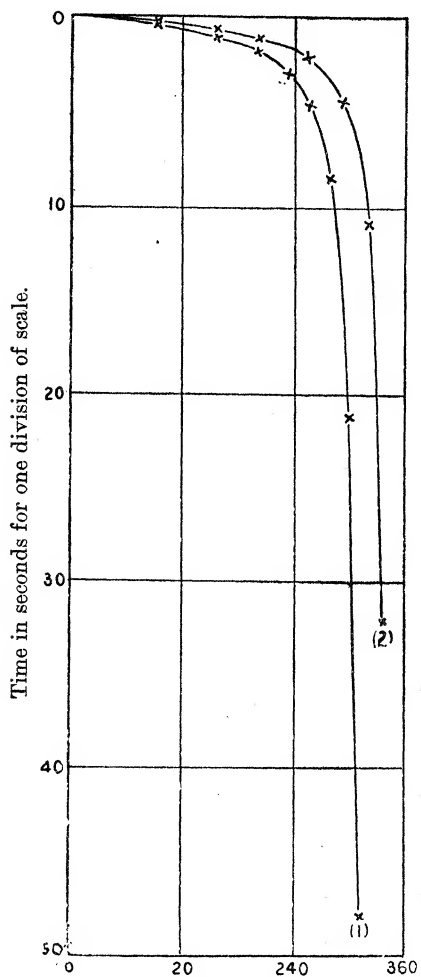


FIG. 2.

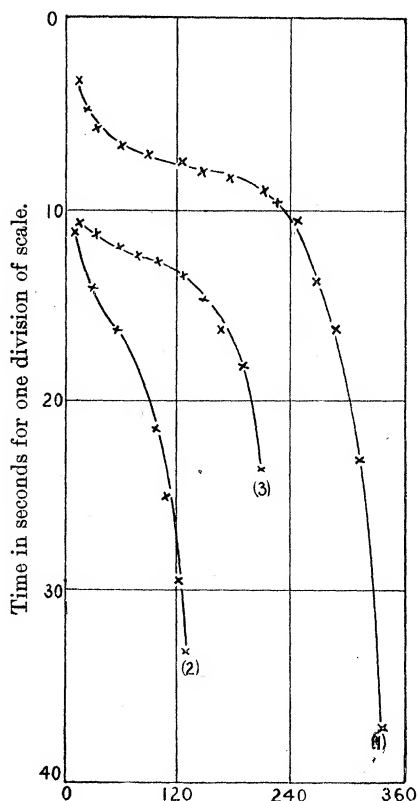


FIG. 3.

have been increased in each case by 10 seconds above the times in Table II, while No. 3, fig. 4, is plotted in half values.

An examination of these graphs shows that at ordinary temperatures (15° C.) there is, except in the case of palladium black, a more or less

pronounced deflection of the curve, not, however, always coinciding with a constant concentration of gas in the metal.

The curves may be considered as composite, two of similar general form being partially superimposed. Thus in the case of thin foil the initial portion may be taken to represent the region where the first curve merges into

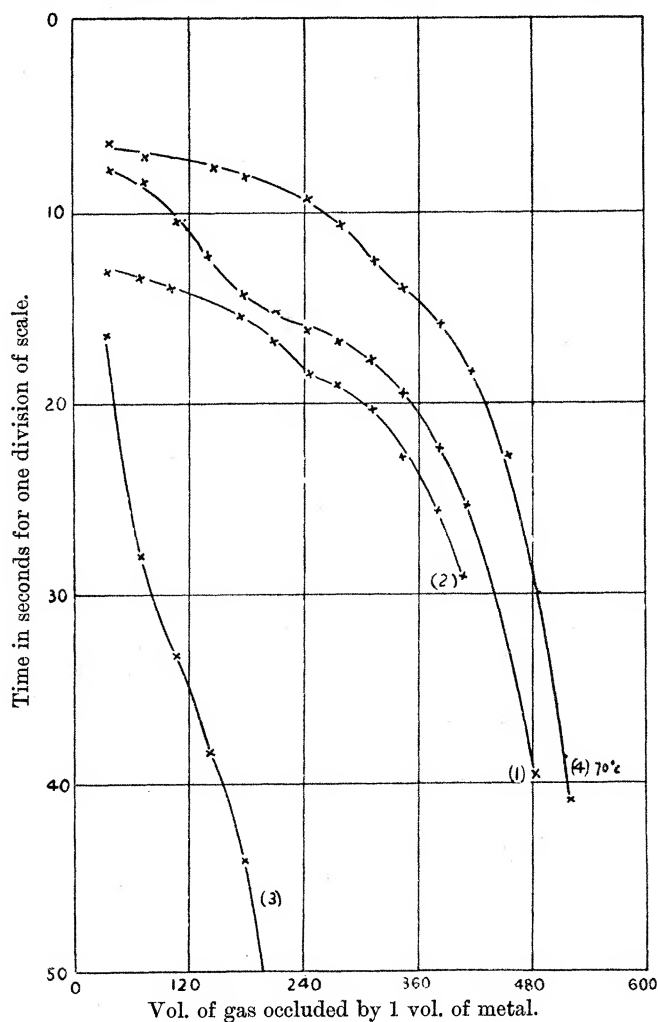


FIG. 4.

the second, the graph consisting almost entirely of this latter, whilst for thick foil, the break between the two curves occurs more towards the centre of the figure.

It could, perhaps, be argued that the change of curvature is so slight that it might well arise from errors in observation, but against this view must be

set the fact that no deflection occurs with palladium black, whereas with the other forms of the metal there is no curve but exhibits it to some extent.

These curves cannot be expressed by any simple formula, but the relation-

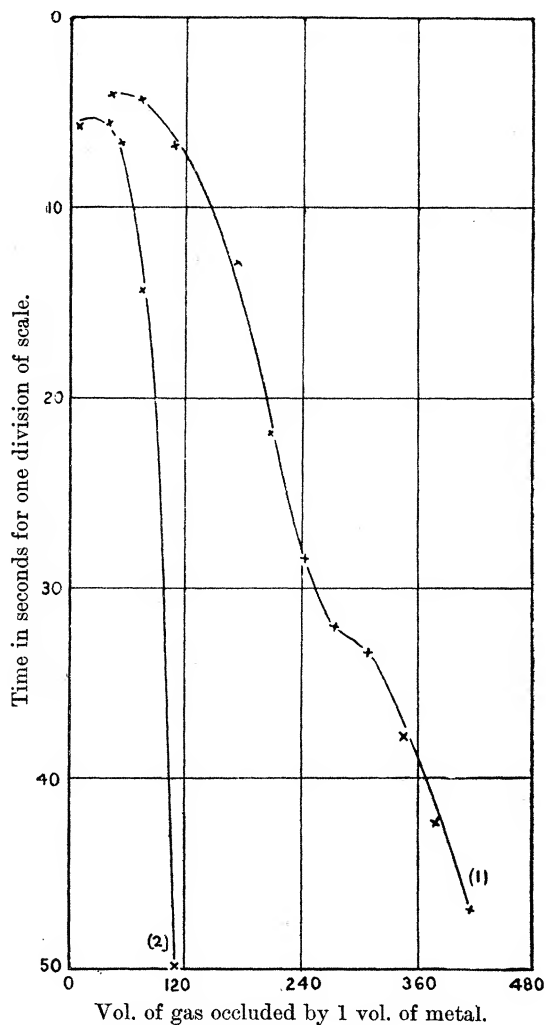


FIG. 5.

ship between the rate of occlusion and the total concentration of gas in the metal appears in general to be represented by such an expression as

$$dc/dt = KC^n$$

where n is not a constant, but varies as a function of C . Neither has n a constant value for any particular form of the metal, for in the tables of rate

values given above it is seen that with the same specimen of metal very different rates are obtained.

This variation of rate for the same sample of palladium is no new observation, but taken in conjunction with the fact that n in the above expression varies also with C , precludes the possibility of representing the curves by any simple expression which has a definite physical meaning.

Since n is not a constant, no information as to the molecular condition of the dissolved gas is obtained from the rate of solution values, but the view of Travers and Zacharias that one is really dealing with a diffusion column appears to receive support. The phenomena can be imagined as follows:—Initially, a certain amount of condensation on the exterior of the metal may take place very rapidly, far too quickly, indeed, to be detected by the methods employed in this investigation. The surface of the metal possessing, however, a very porous and irregular structure, an appreciable time would be taken by the gas to diffuse into its interstices, this diffusion representing the initial portion of the curves for palladium foil. Since, however, after a sufficiently long time has elapsed, gas is found in the interior of the metal, it must be assumed that a more intimate kind of solution must take place immediately beneath the surface. Here the gas would no longer be merely penetrating into the fissures between metallic grains but would be actually entering the grains themselves, passing into solution, for solution and intramolecular diffusion in such a case as this are the same. This would represent the second portion of the rate of solution curves.

For convenience, we may call the initial phenomenon surface diffusion and associate it with α -palladium, and the second solution in the β -metal, and in both cases the rate would diminish with increasing total concentration of gas in the metal, since the smaller and more sinuous the passages became into which the gas was passing, the longer would be the time taken, and to the diffusion effects would be added those of transpiration. A simple logarithmic relation between the rate of solution and concentration of gas within the metal could therefore hardly be expected.

Any attempt to explain the observed phenomena of the rate of solution must, however, take cognisance of the fact that, so far as is known, the pressure-temperature-concentration relations of hydrogen in palladium do not greatly change with different forms of the metal (the experiments of Paal and Germ* on colloidal palladium excepted), and that palladium black is always active towards hydrogen, whereas the stable condition of the crystalline metal is nearly inactive. If, however, to the hypothesis of surface diffusion

* 'Ber.,' vol. 41, p. 805 (1908).

and solution is added that of an α - and β -form of the metal, the observed phenomena can be explained.

In order to account for the constancy of the temperature-pressure-concentration relations, it must be assumed that to each molecule of metal can be associated a certain definite quantity of hydrogen, such quantity varying with the pressure and temperature of the gas. The gas may be regarded as a skin on the metallic particles. Now, if these particles are arranged haphazard, it will be far easier for the gas to diffuse among them and saturate them than if the particles were close packed in some crystalline orientation. In palladium black, which is believed to be amorphous, the particles probably possess little regular arrangement, so the most favourable condition for rapid saturation is presented, and, unless the particles become close packed through crystallisation, there is no reason why the activity or power of rapid saturation of the metal should diminish. The more completely crystalline the metal, the greater should be the difficulty experienced by the gas in entering it, a fact of common observation; α -palladium is therefore imagined as the form with the least regularly orientated and close-packed particles, β -palladium being truly holocrystalline, but the actual phenomenon of solution is the same in either case.

If in palladium black the particles are loosely and irregularly arranged, there would be little, if any, distinction between surface condensation and intramolecular diffusion, the interstices of the surface becoming narrower and narrower and more and more sinuous, till they became spaces between irregularly arranged metallic particles. Hence a rate of solution curve should show no break.

When, however, the gas, after condensing in the surface irregularities, finds itself in contact with metal, the particles of which are in the main close packed, the rate of diffusion would change.

It appears from a large number of experiments that the deflection of the rate curve occurs almost invariably after the metal has been exposed to the gas for about the same interval of time, and that it does not depend on the amount of gas already dissolved. In a series of nine experiments with thick foil, in which the rate of solution varied greatly from one experiment to the next, the time interval before the deflection was found to vary from 13 to 16 minutes, with a mean value of about 15 minutes. Assuming the view that solution of gas depends on the primary saturation of α -palladium, it must be concluded that, after about a quarter of an hour, the rate of solution of gas by the α -form equals the rate at which β -palladium receives gas by diffusion from that variety. If the α -phase was uniformly exposed to the gas at constant pressure, it would acquire a definite saturation in a definite

time, quite irrespective of the amount of phase present, for the actual volume of gas absorbed would increase in direct proportion to the amount of the α -phase.

It is improbable that thermal effects arising from the condensation of the hydrogen have any marked effect under the conditions of the experiment, as, owing to the fact that the bulb containing the metal was kept in circulating cold water, its temperature scarcely rose except during the first two or three minutes.

Turning now to the curves in which the metal was allowed to cool in hydrogen, two distinct types are observed, according as the metal had previously been heated, either *in vacuo* or in the gas. When the metal which has been heated *in vacuo* to a dull red heat, and to which hydrogen has been admitted at this temperature, is allowed to cool in the gas, curves very similar to those already described are obtained. A deflection in this curve has always been observed. When, however, the metal, after previous saturation with hydrogen, is heated and then allowed to cool in the gas, there is no indication in the rate of solution curve of any irregularity. The rate falls extremely rapidly, though after a long enough interval of time the same amount of gas may in each case be retained by the metal.

The hypothesis already put forward provides an explanation of this difference in behaviour. When the metal is heated in the gas, after initial saturation in the cold, hydrogen is evolved, but the palladium still remains saturated, the solubility of gas decreasing with rise of temperature, so that, when the metal is allowed to cool, it is already saturated, though the actual volume of dissolved gas is but small. It appears probable that this gas is dissolved in the β -metal, for on cooling either this saturated palladium, or metal to which hydrogen has been admitted at a dull red heat, the initial portions of the solution curve are very similar, and are characterised by a rapid diminution of rate. Now in this latter case the solution curve again shows a deflection, the phenomena being the same as during solution in the cold, where the α -phase is the initial solvent.

The full cycle of the solution phenomena during heating and cooling may be imagined thus: Palladium in the cold first dissolves gas in its α -, and then in its β -phase. Eventually there is complete saturation. On heating, gas is evolved though the metal remains saturated as regards the β -phase. Solution again occurs in the α -phase on cooling, but the metal already containing a large volume of gas, the diffusion from the α - to the β -phase is so slow that it does not produce any marked irregularity in the rate curve. When, however, hydrogen is initially admitted to the hot metal solution first takes place in the α - and subsequently in the β -phase exactly as during solution in the cold.

If diffusion from the α - to the β -phase is slow under even favourable circumstances, it follows that if the β -phase already contains gas the rate may become almost unmeasurable, for, as has been shown in this communication, a small change of concentration may produce a great change in the rate of solution.

There appears, therefore, every reason to suppose that the solution of hydrogen by palladium is a phenomenon quite analogous to the cases of sorption of gases by other solids, such as charcoal and celluloid, which have already been examined by various authors.

Conclusion.

The rate of solution of hydrogen by palladium is not a simple function of the concentration of gas in the metal. The rate curves consist of two portions (except in the case of palladium black), which have been interpreted as referring to solution in two different forms of the metal. The smooth rate curve for palladium black is taken to mean the almost complete absence of one of these forms.

Note on a Functional Equation employed by Sir George Stokes.

By Sir JAMES STIRLING, F.R.S.

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1. In a paper by Sir George Stokes "On the Intensity of the Light Reflected from or Transmitted through a Pile of Plates,"* the author forms and solves two functional equations, viz.:—

$$\phi(m+n) = \phi(m) + \frac{\phi(n) \{\psi(m)\}^2}{1 - \phi(m)\phi(n)}, \quad (1)$$

$$\psi(m+n) = \frac{\psi(m)\psi(n)}{1 - \phi(m)\phi(n)}. \quad (2)$$

The symbols m , n represent, as was required by the object of the paper, positive integers; but in the course of the investigation he deals with them as continuous variables, solves the equations (1) and (2) on that footing, and finally verifies the equations when m , n are integers. The two equations are treated as independent, and the results are thus expressed,

$$\frac{\phi(m)}{\sin m\beta} = \frac{\psi(m)}{\sin \alpha} = \frac{1}{\sin(\alpha + m\beta)}, \quad (3)$$

* Published in 'Roy. Soc. Proc.' for 1862; see his 'Math. and Phys. Papers,' vol. 4, pp. 145, 148, 149.